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UCRL-CONF-225781

Heterogeneous precipitation of Cu in Fe-Cu alloys

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We are developing models and computational tools for alloys to understand radiation damage in nuclear materials

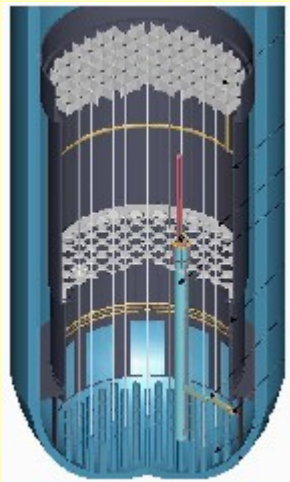
Motivation

- Copper is found as an impurity in reactor pressure vessel steels
- Radiation induced Cu precipitation leads to changes in the microstructure and controls damage effects such as embrittlement and radiation hardening

Nuclear materials

Microstructural evolution of structural steels under irradiation

Reactor Pressure Vessel

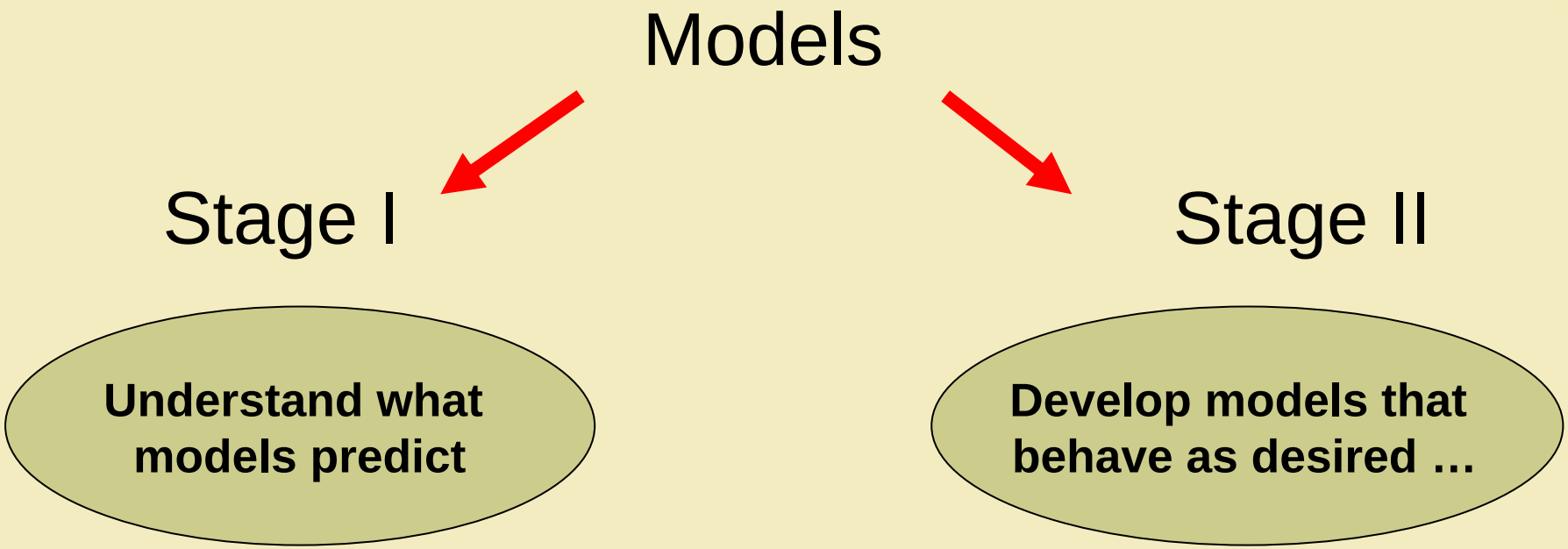


www.tecnatom.es/english/catalogo

We investigate the formation of Cu precipitates in Fe-Cu alloys of low Cu concentration using :

- a classic potential that has been fully characterized thermodynamically
- a parallel Monte Carlo code with displacements that allows to perform simulations of heterogeneous precipitation

Classic interatomic potentials for MD / MC simulations in alloys



Our objective is to relate *ab initio* energetics, alloy potentials, thermodynamics, and microstructures

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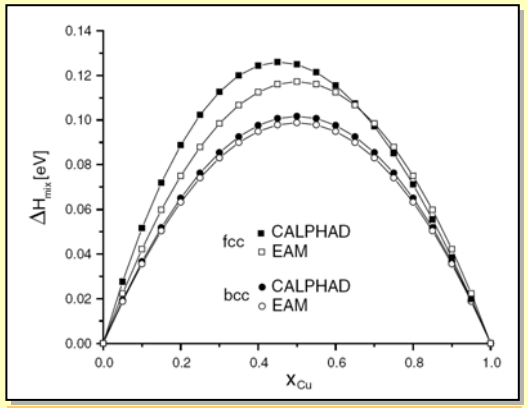
1 *ab initio* ⟺ potentials

- **A methodology to generate classic potentials able to reproduce formation energy of complex alloys**

JNM 349, 317 (2006)



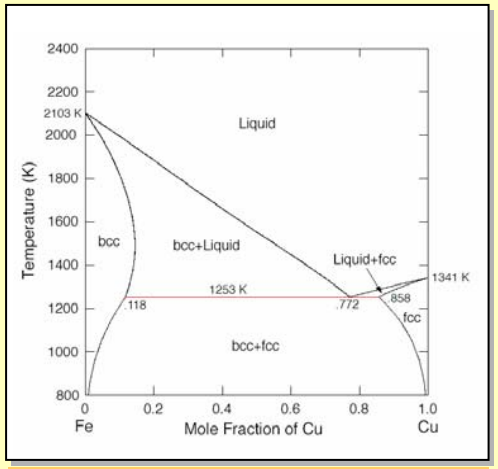
Excess enthalpy of mixing at 0 K for both fcc and bcc FeCu solid solutions

2 potentials ⟺ thermodynamics

- **A unique suite of codes to evaluate free energies:**

  an *entropy - meter*

Phys. Rev. B 66, 054201, (2002)
Phys. Rev. B 68, 214205, (2003)

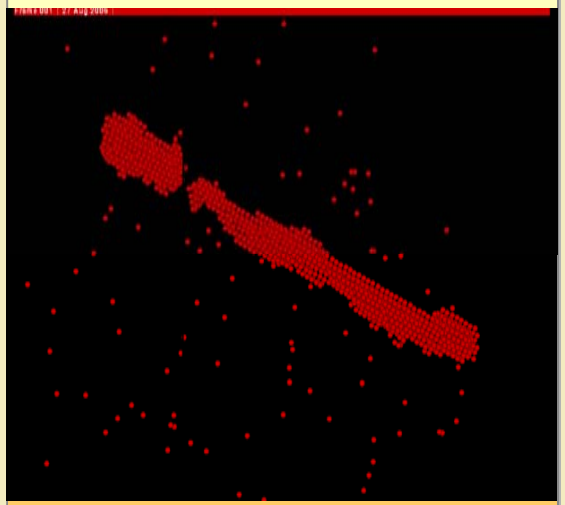


Phase Diagram of EAM FeCu

3 potentials ⟺ microstructure

- **A powerful massively parallel Monte Carlo code with displacements to study heterogeneous precipitation**

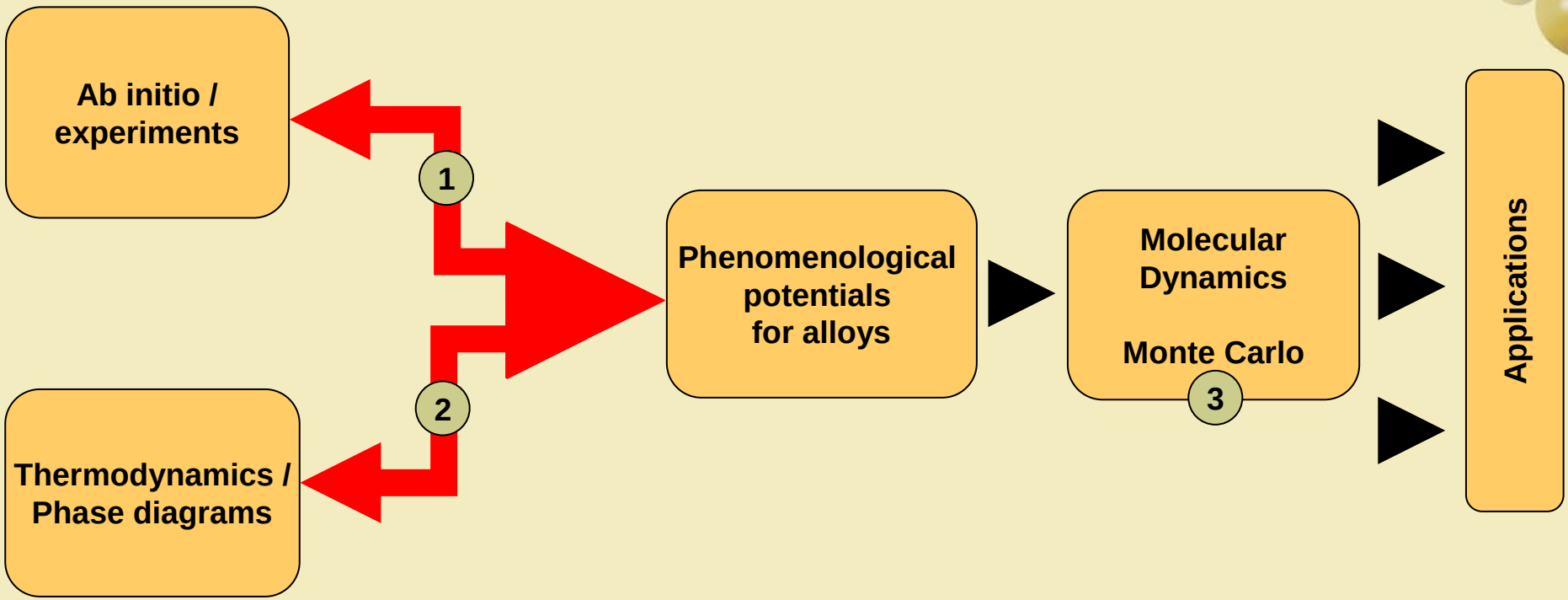
Appl. Phys. Lett. 87, 231904 (2005)



Cu precipitates on screw dislocation

We work on:

1. New approach to generate potentials for alloys
2. Thermodynamic package
3. Parallel Monte Carlo code w/displacements



② Computational Thermodynamics

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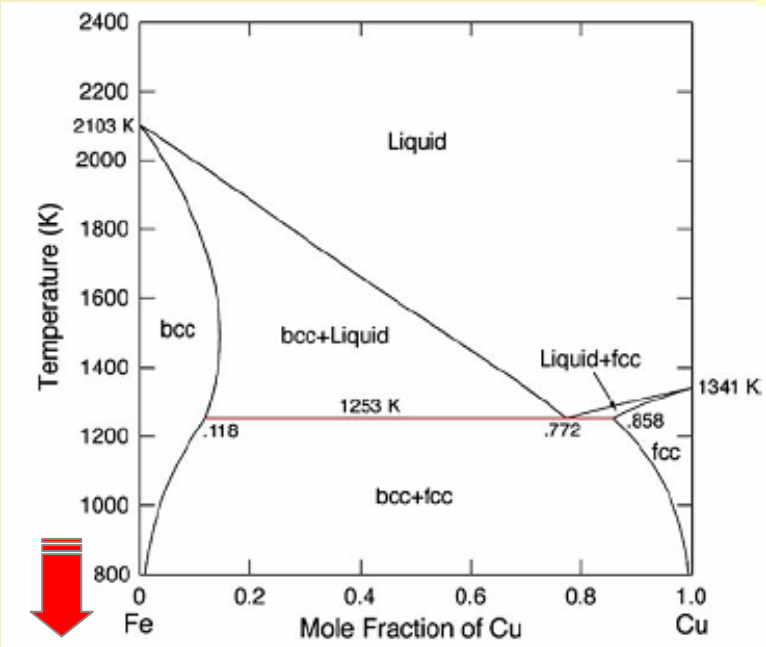
We evaluate free energies

$$F = -kT \ln\left(\int_{\Omega} \exp\left(-H(x)\right) dx \right)$$

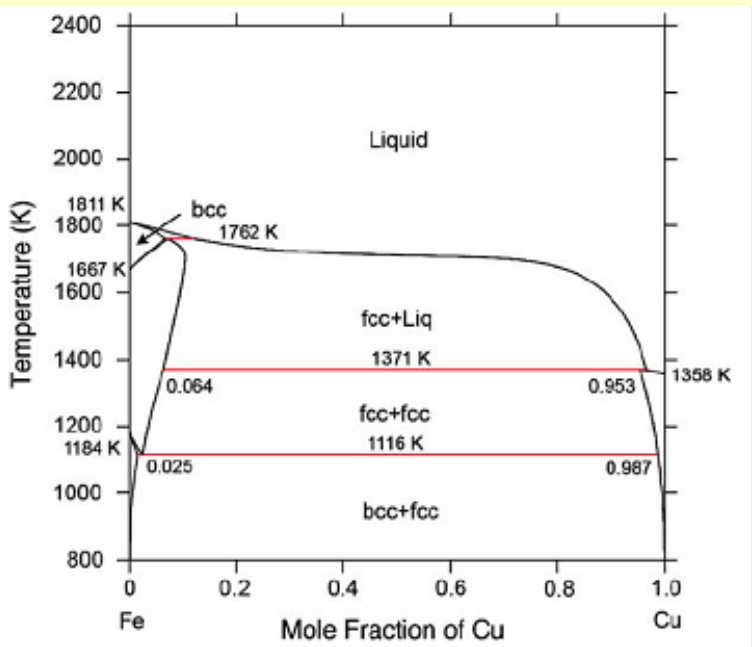
Switching Hamiltonians
Gibbs – Duhem integration
Gas expansion
…

Phys. Rev. **B 66**, 054201, (2002)
Phys. Rev. **B. 68**, 214205 (2003)
J. Nuc. Mat. **336**, 233 (2005)
J. Nuc. Mat. **349**, 317 (2006)

Phase diagram corresponding to
Ludwig-Farkas Fe-Cu EAM Potentials



CALPHAD Fe-Cu Phase Diagram
Experiment



Region of nuclear interest

We developed a massively parallel displacement Monte Carlo code to predict microstructures

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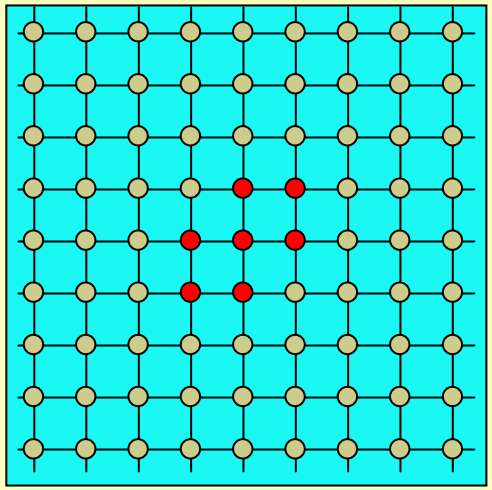
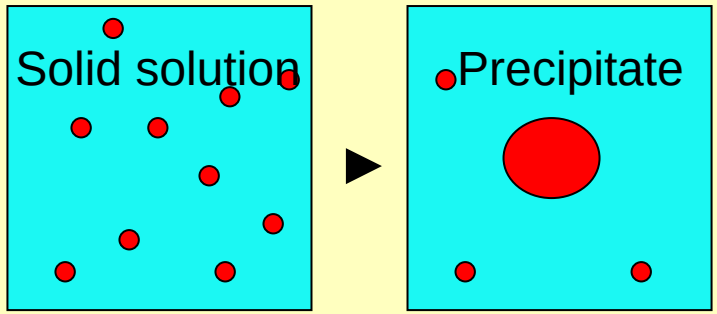
Lattice Monte Carlo



$\Delta G = -V\,\Delta E + A\,\gamma'$

Monte Carlo with displacements



G_1

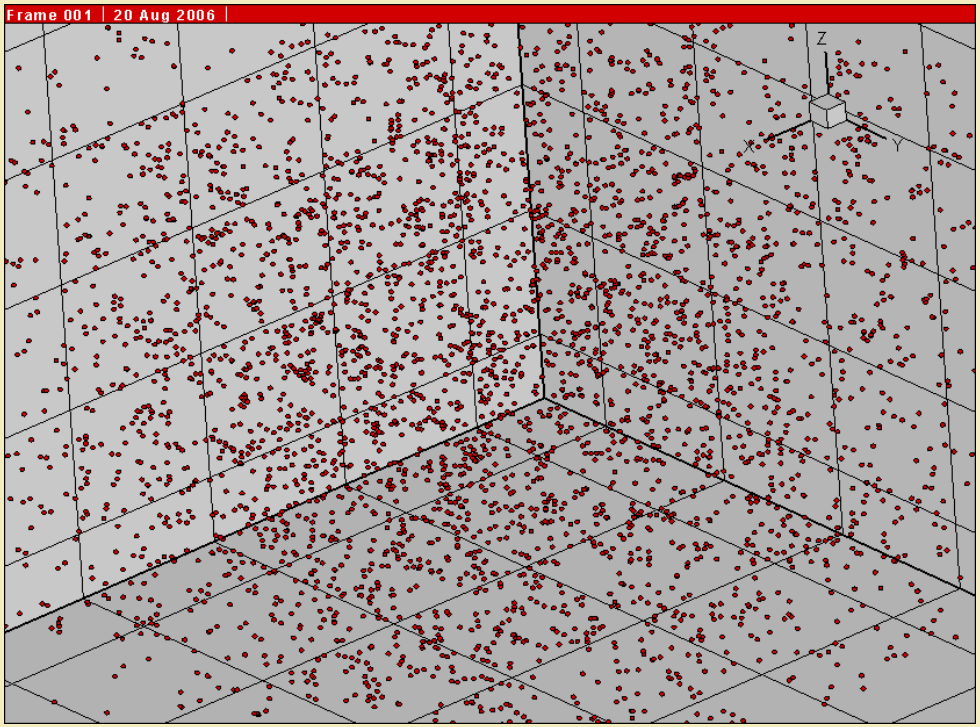
$\Delta G = G\beta - G\alpha$

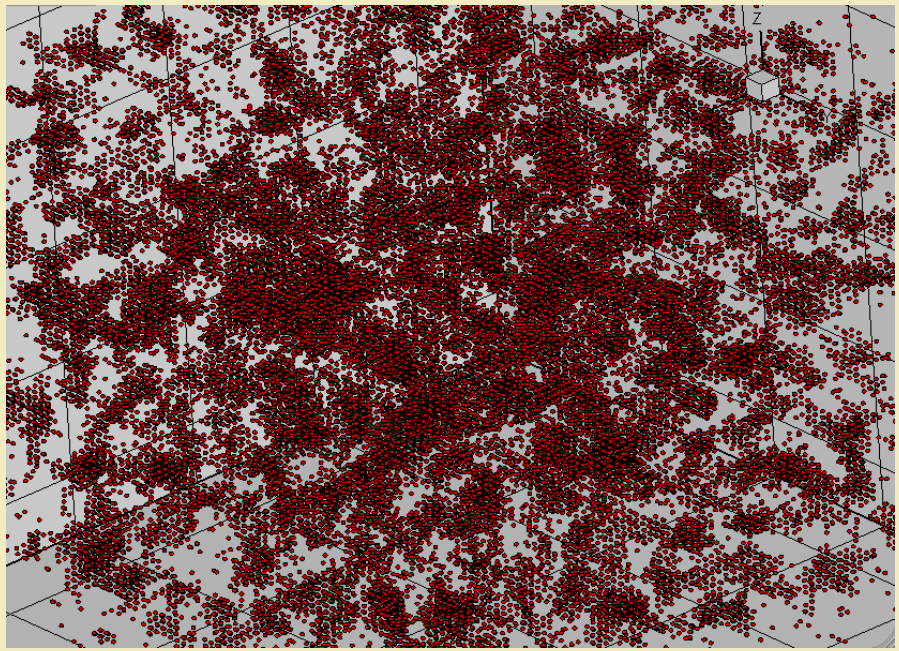
$\Delta G = -V\,(G_\beta - G_\alpha) + A\,\gamma + V\,\Delta G_{el} + V_{Ext}$

lattice ← **Monte Carlo** → displacements

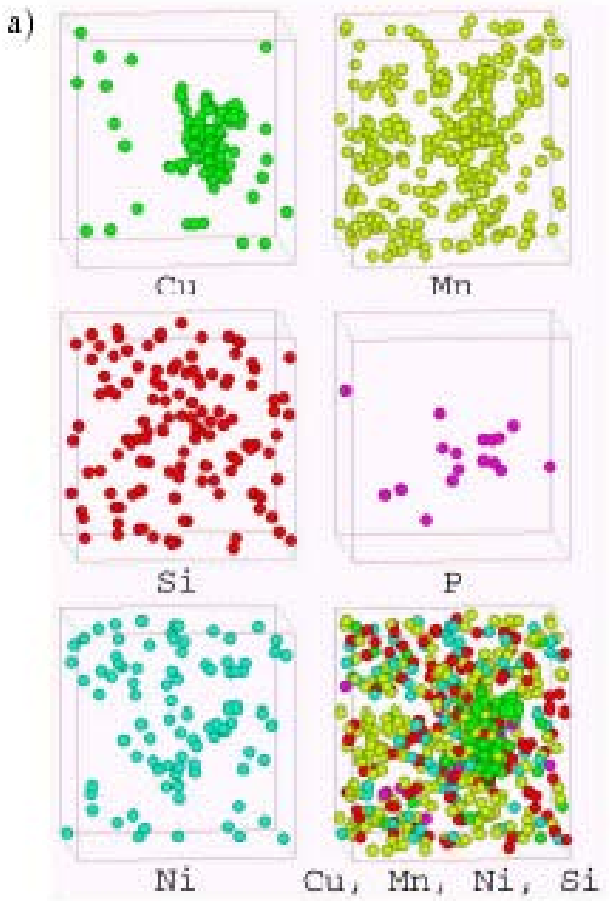
While lattice MC gives time evolution (k-MC), it does so at the price of neglecting several terms in the driving force

Homogeneous Cu precipitation





Experimental determination of cluster composition in industrial ferritic steel



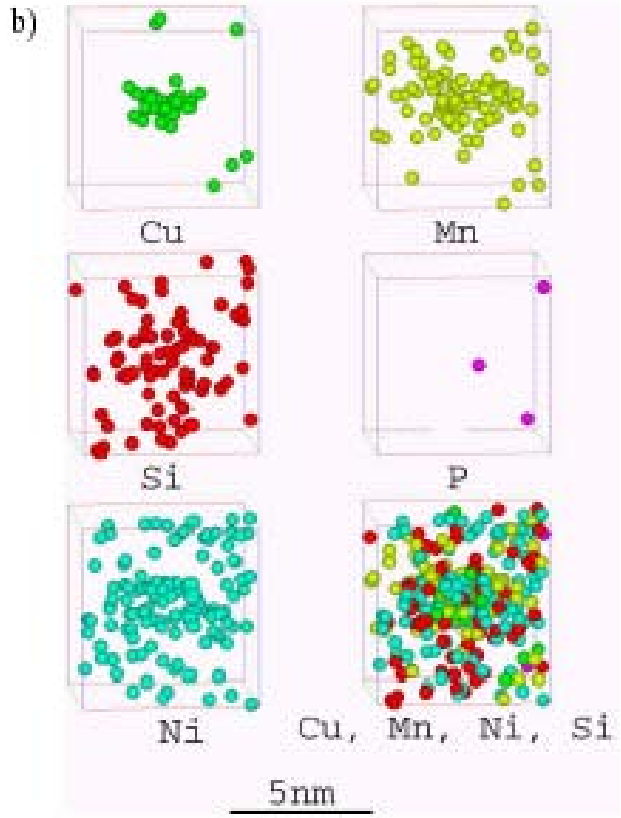
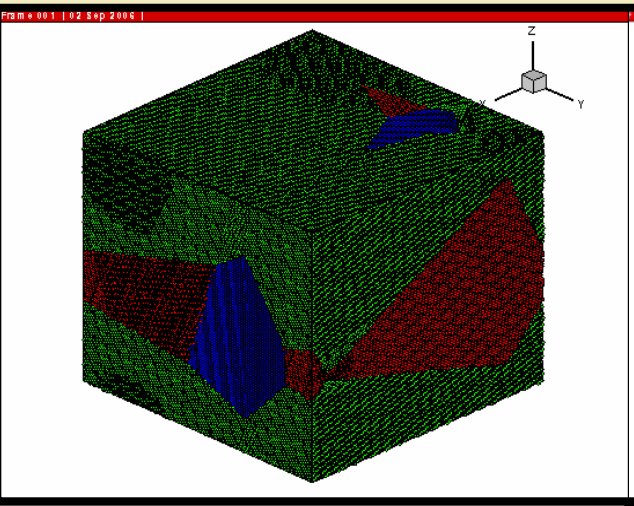
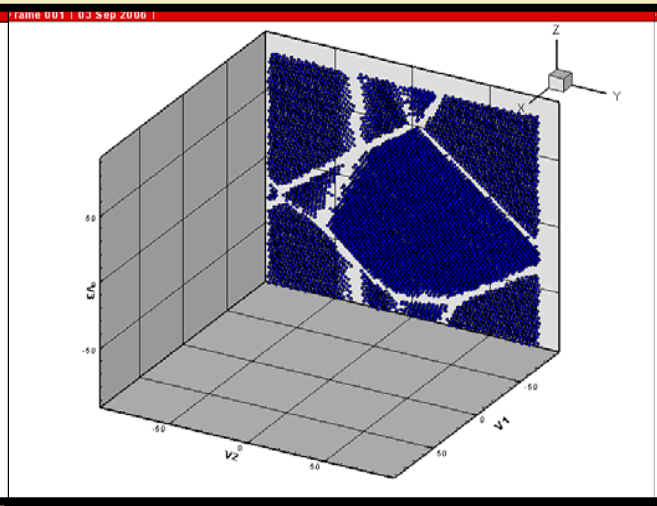


Figure 2. *Enlarged view of a) cluster 2 (extents of outline box 8x8x8nm^3) from 3DAP analysis of SH and b) cluster 8 from 3DAP analysis of WV012 (extents of outline box 6x6x6nm^3) showing distribution of Cu, Mn, Ni, Si and P.*

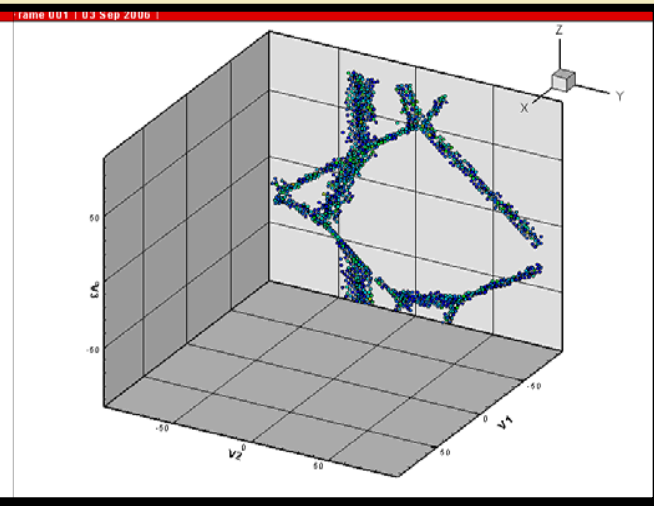
Strategy to show you several HETEROGENEOUS precipitation examples: a nanophase Fe sample



Nanophase sample
2 M atom, 15 grains

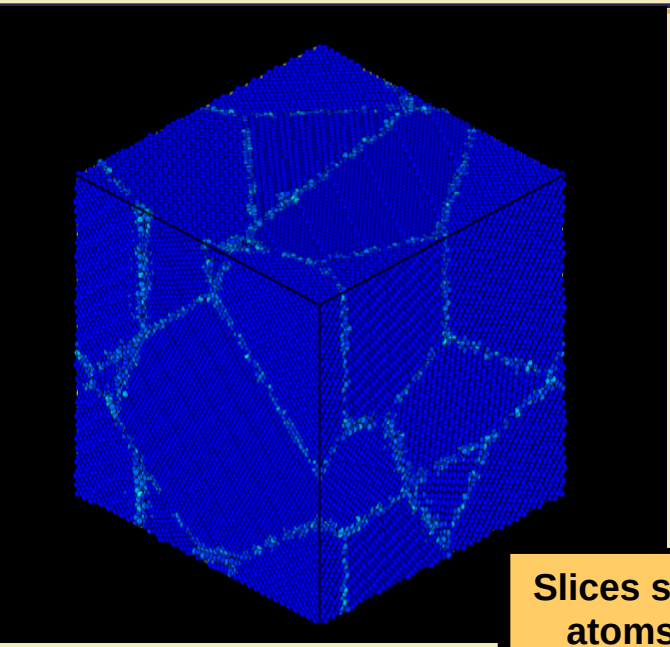


Slices showing perfect crystal bcc atoms



Slices showing grain boundary atoms

Heterogeneous precipitation in Fe-Cu



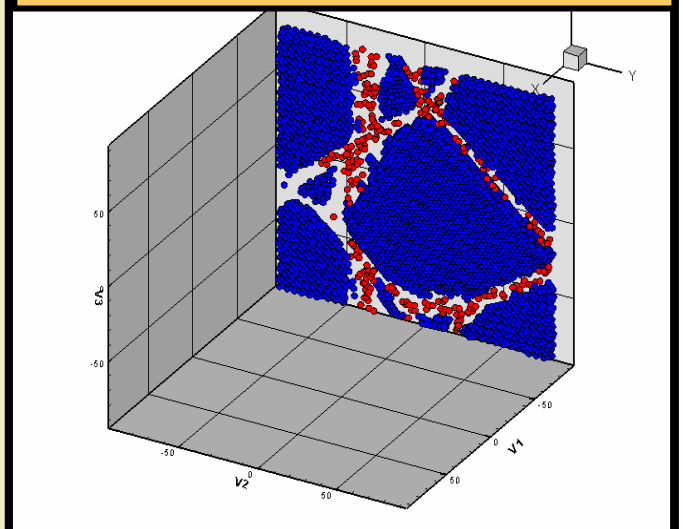
Bulk nanophase material

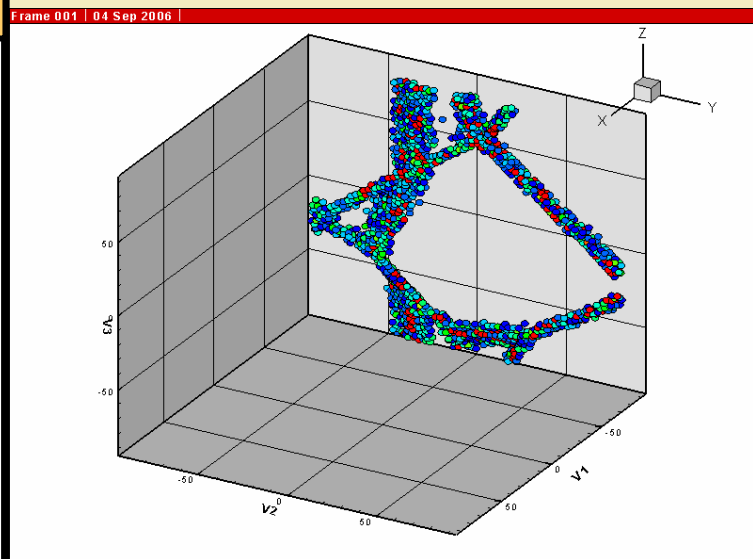
Cu has a strong tendency to precipitate

- **at grain boundaries**
- **at junctions**

3% Cu precipitation at grain boundaries in Fe

Slices showing perfect crystal bcc atoms in blue, Cu atoms in red





Heterogeneous Cu precipitation in the presence of a free surface

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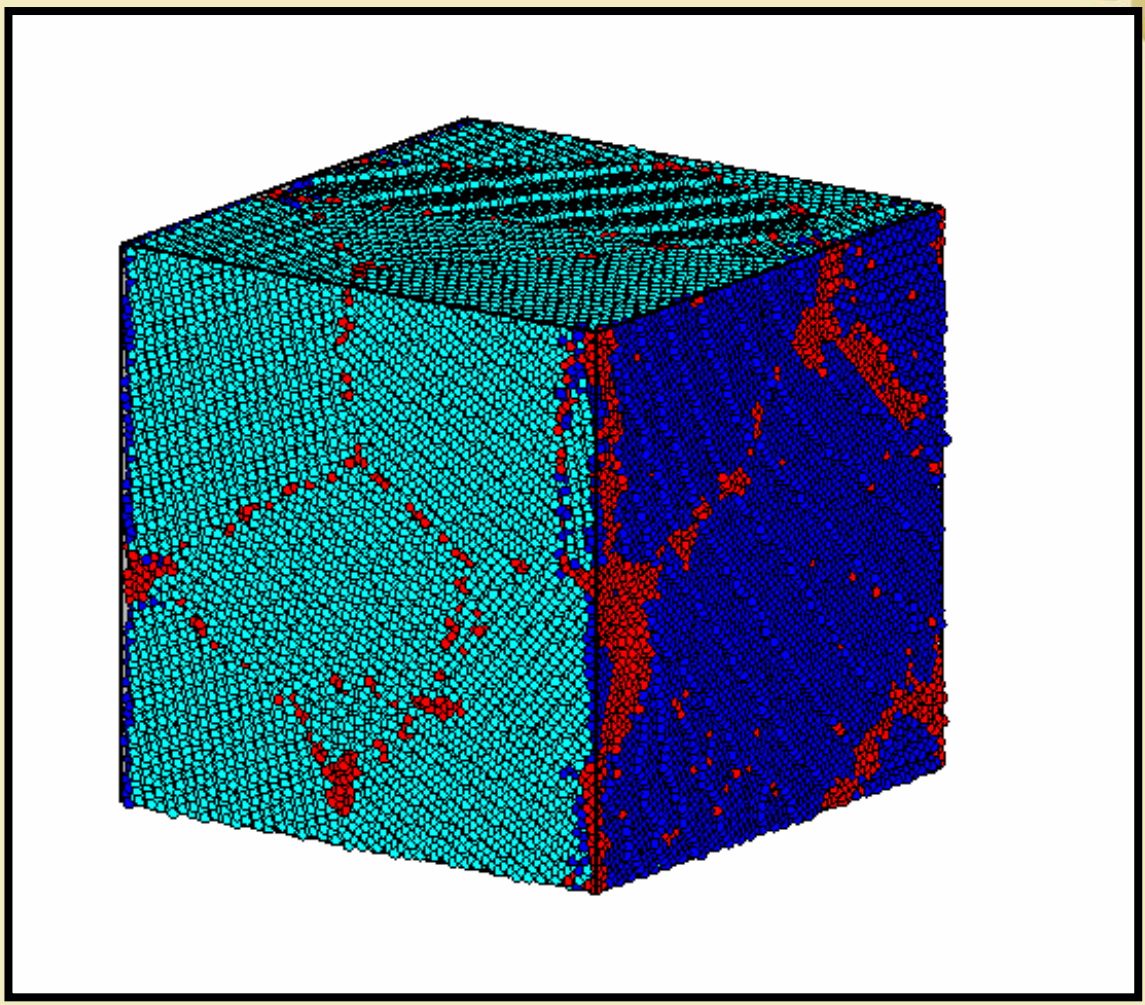
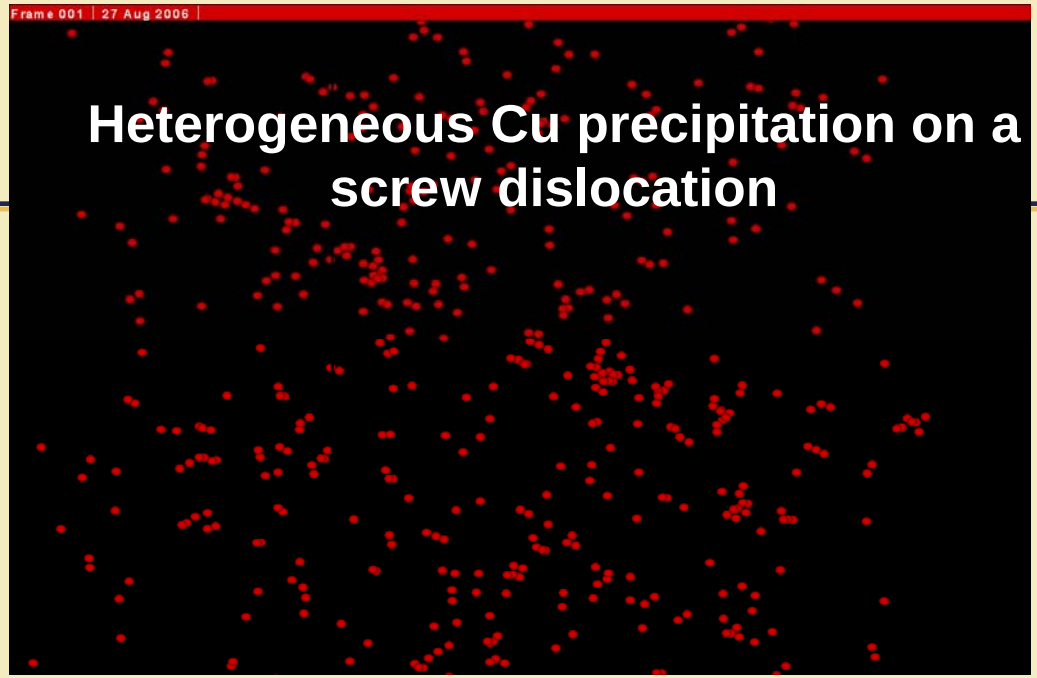
Free surface (dark blue) in a nanophase sample

Cu goes preferentially to grain boundaries and triple-junctions that emerge at free surfaces



Heterogeneous Cu precipitation on a screw dislocation



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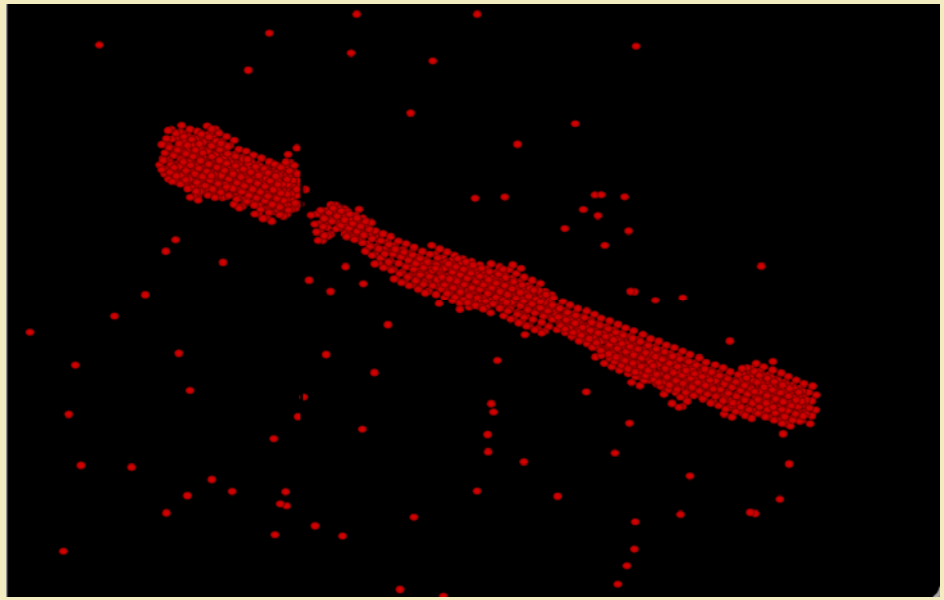
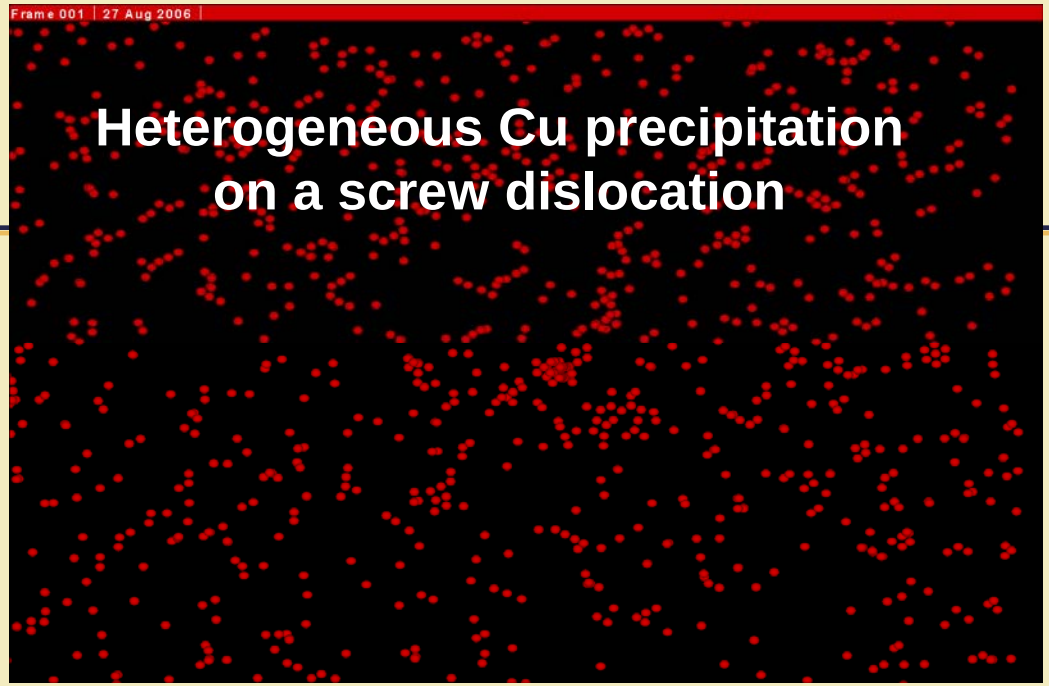
3% Cu precipitation at the core of a screw dislocation in Fe





Heterogeneous Cu precipitation on a screw dislocation

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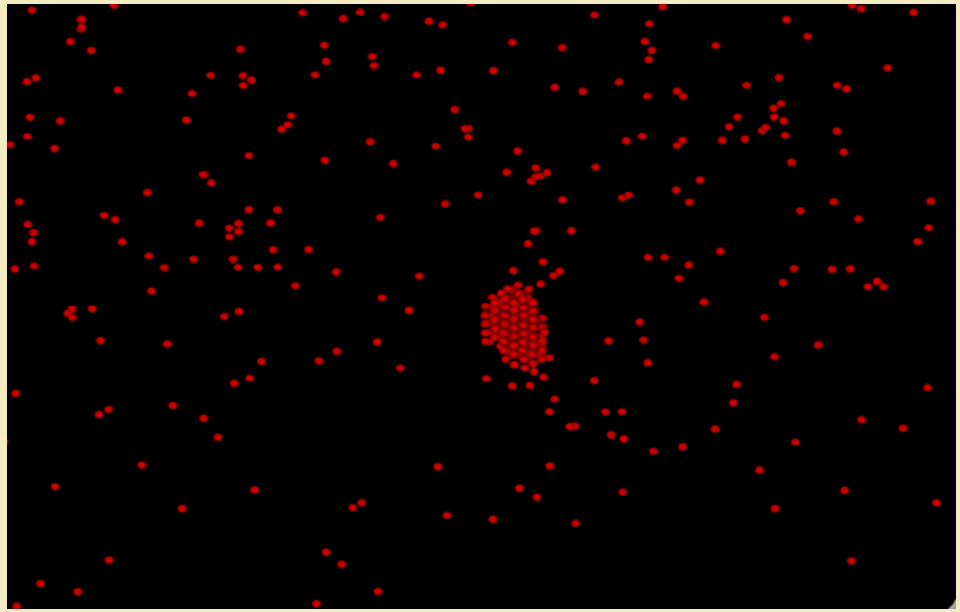

Frame 001 | 27 Aug 2006

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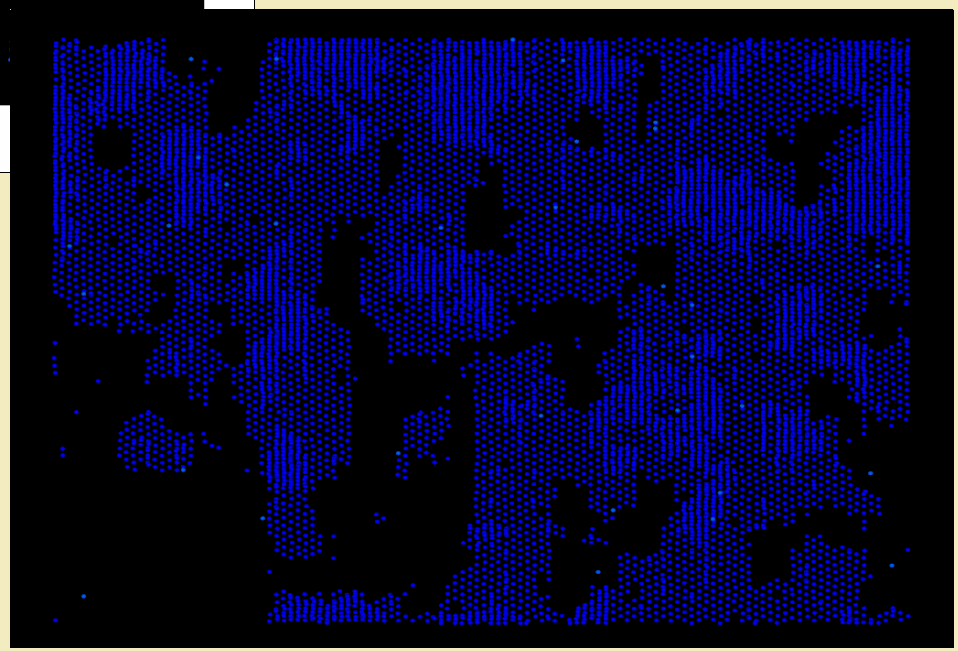
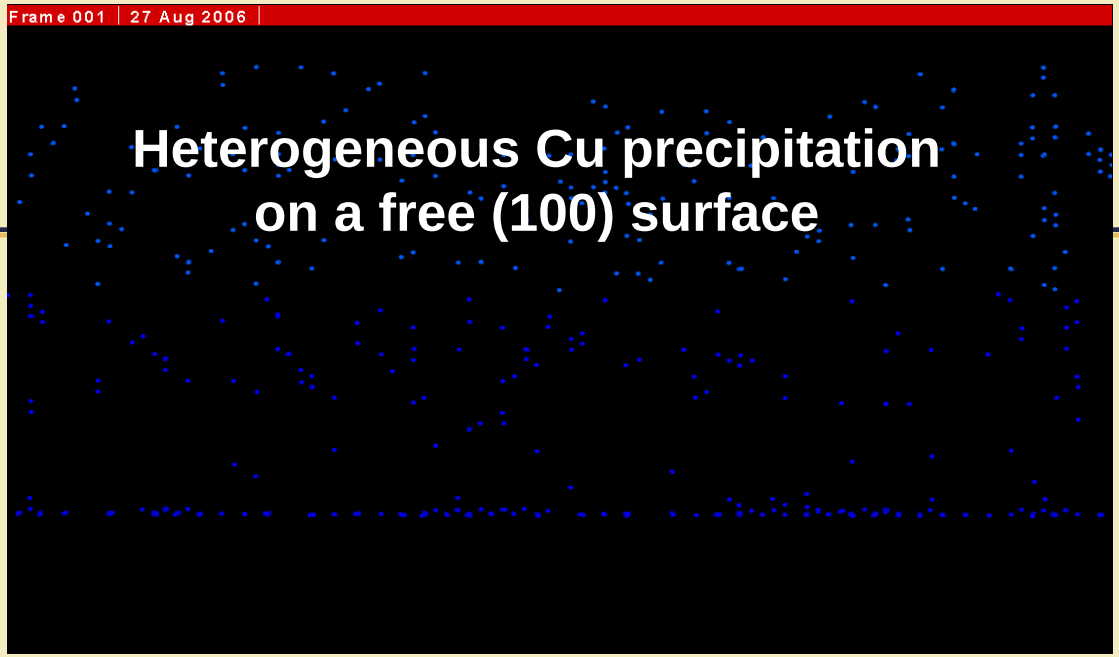
Heterogeneous Cu precipitation on a free (100) surface





Heterogeneous Cu precipitation on a free (100) surface

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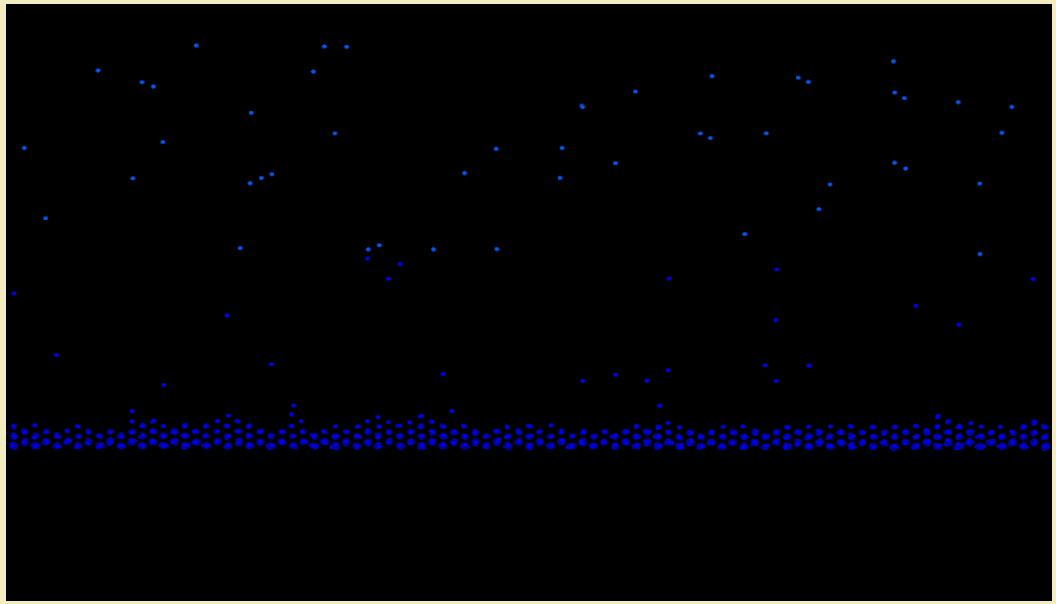

Conclusions:
New models and tools for computational modeling of alloys

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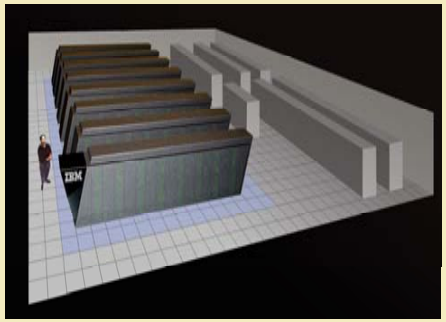
Developments:

1. ✓ Formalism to design classic potentials for complex alloys
2. ✓ Thermodynamic package to evaluate free energies of alloys in any phase
3. ✓ Parallel Monte Carlo code with displacements, to predict equilibrium microstructures in alloys

Applications:

✓ An accurate description of the thermodynamics of the system allows us to study heterogeneous precipitation and obtain physically based microstructures

✓ We are studying the effect of precipitation on mechanical properties



Computational Materials Science